INDEPENDENCE MALL WEST PHILADELPHIA, PA. 19105 TELEPHONE (215) 592-3000

REPLY TO:
BOX 219
BRISTOL, PA. 19007
(215) 788-5501

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135266

ROHM AND HAAS COMPANY

June 25, 1968

Received

Mr. Herbert A. Howlett
Chief Engineer
Delaware River Basin Commission
P. O. Box 360
Trenton, New Jersey 08603

Dear Mr. Howlett:

In our discussion with you prior to the afternoon meeting of the Delaware River Basin Commission on May 22, you gave Mr. Rarig and me three questions upon which it would be desirable to have information. The questions concerned the arsenic in the stream bottom muds; the effect of acid conditions on the arsenic present in the stream waters and whether or not ingested pentavalent arsenic is converted by the body to the toxic trivalent form. We have done a considerable amount of laboratory and literature survey work since then in an attempt to get enough information in a limited period of time to reasonably answer these questions. We are pleased to forward the reports of this work to you.

Enclosure number one is a table showing the total arsenic content of earth collected along the Tulpehocken Creek and the Schuylkill River in addition to the bottom samples which were reported previously to you on May 22. All of the samples including those from above the flood plain; show the presence of arsenic. This indicates that the origins of the arsenic in bottom samples, other than the Myerstown Plant area and vicinity; probably include natural and agricultural sources.

Enclosure number two is a laboratory report by Mr. N. T. Chamberlain and Mr. H. Behrend showing the results of their work of determining the affinity of arsenic for mud. In all their experiments, arsenic showed a definite affinity for mud. The mud reduced the arsenic content of water to trace amounts and retained it even when the mud contained substantial quantities in which case releasing it to only trace levels in the water. As a result of this work, we believe the great bulk of the arsenic found in the stream bottom muds is arsenic which was ad/absorbed from water by suspended settleable matter, particularly during periods of surface runoff and bottom shifting when flows were high. It is our opinion ..., that precipitation of arsenic from the hard water wells at Whitmoyer in the hard water streams in unlikely.

AR100146

Enclosure No. 3 is a laboratory report by Mr. J. M. Kauffman showing the forms of arsenical content of the well waters. The first two samples reported are duplicates of those you got in preparation for your trip to Cincinnati. Wells 3 and 4 contained the highest concentrations of tri-valent arsenic. The wells away from these two wells including new wells have relatively small concentrations of the tri-valent arsenic. Wells 3 and 4 are located at the arsenical manufacturing building and this may be from past leakages of untreated wastes. The floors were rebuilt and sealed and the floor trenches lined with locked-in stainless steel liners in February, 1965. This and other containment facilities have been maintained since then to prevent spills, seepages and leaks to the outside from current production operations. Mr. Kauffman's group has been also working on determining the forms of arsenic present in the stream bottom samples. However, difficulties have been experienced in extracting the arsenic unchanged in form from the mud and results are not sufficiently reliable to report at this time. The work is being continued.

Enclosure No. 4 is a report by Dr. J. B. Graham giving a description of the geological setting of the Tulpehocken Creek watershed with respect to ground water movement. It is Dr Graham's opinion that a ground water divide or hydraulic barrier does exist in the vicinity of the Womelsdorf area which prevents eastward continuation of ground water flow. Thus, this water is forced to the surface as a source of supply to the Tulpehocken Creek along its banks, etc, westward of the barrier.

Enclosure No. 5 is a telephone report to me from Mr. Kauffman of the results obtained from acidifying arsenic bearing waters to pH 3. The data indicates that the organically bound arsenic and the inorganic pentavalent arsenic is unaffected by low pH and that the inorganic trivalent arsenic tends to oxidize to the pentavalent form.

Enclosure No. 6 is a report of a literature survey made by Dr. W. P. Campbell. In essence, it has been found that pentavalent arsenic is not reduced to the trivalent form in animals and thus is excreted as such rather rapidly. The belief that pentavalent arsenic is toxic because it is reduced to the trivalent form is believed speculative since it is not supported by any data or references. Recent data suggests trivalent arsenic is slowly oxidized to the pentavalent state in the body so it can be excreted.

Very truly yours,

T. Iezzi

bnm
Attachments

ENCLOSURE NUMBER 1

ANALYSIS OF EARTH AND STREAM BOTTOMS SAMPLES FOR ARSENICAL CONTENT
TULPEHOCKEN CREEK AND SCHUYLKILL RIVER

May, 1968

			Total Arsenic Content		
Sample Number	Stream	Location	Earth from Approx. 500 Ft. from Est. Flood Stage Line PPM	Earth from Stream Bank Approx. 6 Ft. from Waters Edge PPM	Stre Bott
1	Tulpehocken Cr.	0.5 Mile West (upstream) of Whitmoyer Plant	3.7	4.3	3.
2	Canal	North of Concrete Vault at Whitmoyer Plant	5.3	1100	128
3	Tulpehocken Cr.	100 Yds. East (downstream) of Whitmoyer Plant	8.8	28	170
4	Tulpehocken Cr.	College St. Bridge Meyerstown	5.6	65	81
5	Tulpehocken Cr.	Millardsville	14.9	16	73
6	Tulpehocken Cr.	Route 422 Bridge at Womelsdorf	4.3	103	36
7	Tulpehocken Cr.	2 Miles East of Bernville	2.4	8.4	
8	Tulpehocken Cr.	1 Mile upstream of Confluence with Schuylkill River	6.7	4.7	26
9	Schuylkill River	1 Mile North (up-stream) of mouth of Tulpehocken Creek	5.4	5.3	4
9A	Schuylkill River	3 Miles North (up-stream) of mouth of Tulpehocken Creek	5.7	4.8	4.8
10	Schuylkill River	1 Mile South (down-stream) of mouth of Tulpehocken Creek	7.2	17.7	12
11	Schuylkill River	200 Yds. above intake of Pottstown Water Fil-tration Plant	14.2	10.3	12

Note 1: Bottom samples were collected at midstream with the exception of the Schuylkill River which were taken six feet from the shore line.

Note 2: The earth samples were collected both within the flood plain at a point on the stream bank approximately 6 feet from the normal waters edge and outside the plain at point 500 to 1000 feet from the high water mark which was approximated by eye sight.

AR100148

May, 1968

Note 3: Samples were collected to a depth of 3 to 4 inches. Gravel and debris were excluded and the remaining soil mixed prior to analysis.

Note 4: The samples were digested with sulfuric acid and nitric acid to extract and convert all arsenical materials to arsenic before proceeding with standard analytical procedure for arsenic.

Note 5: Analyst, Mr. N. T. Chamberlain, reported he had checked analytical procedure with good results. He recovered 28.8 PPM arsenic from a soil sample he had "spiked" with 30 PPM.

T. Iezzi

bd

ENCLOSURE NUMBER 2

Copies: Mr. R. J. Anderson
Mr. W. F. Bartoe
Dr. W. B. Campbell
Dr. B. Gutbezahl
Dr. C. L. Levesque
Writer

Bristol, Pennsylvania
June 19, 1968

MEMO TO: Mr. T. Iezzi

FROM: H. Behrend

SUBJECT: Schuylkill River Samples - Arsenic Content

REFERENCE: NTChamberlain/HBehrend, 6/19/68

The work assigned to Laboratory 2 relating to arsenic discharge at the Whitmoyer Plant has been completed. The attached reference adequately describes the various samples and experiments which were involved and reports the data observed. In all cases, the arsenic shows a definite affinity for the mud.

Herman Behrend
Herman Behrend

ldm

Attachment

AR100150

cc: Writer

Bristol, Pennsylvania
June 19, 1968

MEMO TO: Mr. Herman Behrend

FROM: N. T. Chamberlain

SUBJECT: Schuylkill River Samples - Arsenic Content

At your request, mud samples from the Schuylkill River were analyzed for arsenic content by Test Method 966-3, "Determination of Arsenic". In addition, experiments were conducted to determine the relative affinity of arsenic for river water and mud. All samples were prepared by acid digestion and, where necessary, filtered before analysis. Terms used throughout are defined below.

Terms

#8 Mud - Schuylkill River bottom, one mile before confluence of Tulpehocken Creek

#10 Mud - Schuylkill River bottom, one mile after confluence of Tulpehocken Creek

Dry Mud - The above samples oven dried at 105°C for 90 minutes.

Normal Water - Low arsenic water composed of six parts Schuylkill River water and one part Tulpehocken Creek water

High Arsenic Water - Composite of well waters from area of Whitmoyer Plant (Diluted to 9.1 ppm arsenic with normal water for use in Experiment #4)

Blank values were determined on all the above defined materials for total arsenic. The results are located in the attached table under Experiment #1.

Recovery values from mud samples and normal water are found under Experiment #2.

Experiments #3 to #6 were conducted by preparing a 10% slurry (20 grams mud and 180 grams water) for each test and mechanically shaking it for 48 hours. Water and mud layers were separated by centrifuging and analyzed as above.

Experiment #3 shows distribution of arsenic between mud and normal water.

Experiment #4 shows distribution of arsenic between #8 mud and high arsenic water.

AR100151

NTChamberlain/HBehrend
June 19, 1968
Schuylkill River Samples
Arsenic Content

Experiment #5 shows effect of pH on distribution of arsenic between #10 mud and normal water. (Acidified with sulfuric acid to pH = 3)

Experiment #6 is a repeat of Experiment #3 using mud portions which were oven dried before the slurry was prepared.

Norman T Chamberlain
Norman T. Chamberlain

ldm

Attachment

ARSENIC IN MUD AND RIVER WATER*

Exp. No.	Sample		Arsenic Added PPM	Arsenic Added MMG	Arsenic Found PPM	Arsenic Found MMG	Correction For Blank MMG	Net Found MMG	Recovery %	Distribution** %
1	**BLANK VALUES**		-	-	-	-	-	-	-	-
	Normal Water		-	-	< 0.1	-	-	-	-	-
	High Arsenic Water		-	-	123	-	-	-	-	-
	No. 8 Mud (as is)		-	-	4.7	-	-	-	-	-
	No. 10 Mud (as is)		-	-	19.7	-	-	-	-	-
	No. 8 Mud (Dry)		-	-	5.25	-	-	-	-	-
	No. 10 Mud (Dry)		-	-	19.5	-	-	-	-	-
2	**RECOVERY VALUES**									
	Normal Water		5.0	50	4.9	49	-	49	98	-
	No. 8 Mud (as is)		10.0	100	12.0	120	46.5	73.5	74	-
	No. 10 Mud (as is)		10.0	100	26.7	267	197	70.0	70	-
	MUD-WATER EXTRACTIONS		**Arsenic Present**		**Arsenic Found**					
3	No. 8 Mud (as is) + Normal Water	Mud	4.65	93.0	4.1	82.0	-	82.0	-	89
		Water	< 0.1	-	< 0.1	-	-	-	-	-
	No. 10 Mud (as is) + Normal Water	Mud	19.7	394	13.0	260	-	260	-	66
		Water	< 0.1	-	0.21	38	-	38	-	10
4	No. 8 Mud (as is) + Arsenic Water	Mud	4.65	93.0	70.0	1400	-	1400	-	77
		Water	9.1	1730	0.20	36	-	36	-	2
5	No. 10 Mud (as + Normal Water (pH 3)	Mud	19.7	394	13.2	264	-	264	-	67
		Water	< 0.1	-	0.21	38	-	38	-	10
6	No. 8 Mud (Dry) + Normal Water	Mud	5.25	105	4.2	84	-	84	-	80
		Water	< 0.1	-	<0.1	-	-	-	-	-
	No. 10 Mud (Dry) + Normal Water	Mud	19.5	390	22.8	456	-	456	-	116
		Water	<0.1	-	<0.1	-	-	-	-	-

*All Analytical Data Are The Average of Two Determinations.

Repeatability ± 5%, relative

**Based On Total Arsenic in the Slurry.

MEMO

WHITMOYER LABORATORIES, INC.

MYERSTOWN, PENNA., U. S. A.

cc:
WPA
FAD
PAH
GAT
Water File

Date June 21, 1968

To Mr. Tom Iezzi

From Mr. J. M. Kauffman

DATE STAMP

Subject: DETERMINATION OF ARSENIC CONTENT OF WELL WATERS

Five samples of water, representing various wells or composites of wells in the vicinity of the Whitmoyer property were analyzed for organic arsenic as well as trivalent and pentavalent inorganic arsenic. The results obtained are given in the attached table.

The total arsenic was determined on a digested sample by the colorimetric diethyldithiocarbamate procedure. The total inorganic arsenic was determined in the same manner but without digestion of the sample.

The trivalent and pentavalent arsenic were determined independently on a separate portion of the sample. After removal of the organically bound arsenic by ion exchange, the trivalent arsenic content was determined iodimetrically and the pentavalent arsenic by a spectrophotometric method.

The analyses were performed by Messers Moore and Lash with Mr. Lash assembling and evaluating the data.

John M. Kauffman

John M. Kauffman

JMK/nlk

Lab T-187-192
RPL 3/113-117 3/119-127

AR100154

Identification	Lab No.	Organic Arsenic ppm	Organic Arsenic %*	Inorganic Arsenic As+5 ppm	Inorganic Arsenic As+5 %*	Inorganic Arsenic As+3 ppm	Inorganic Arsenic As+3 %*	Total Arsenic (1)
Wells 2 & 6	T-187	4	3.3	105	89.0	9	7.6	118
Wells 3,4,5,6 & 7	T-188	25	24.0	8	7.6	71	68.3	104
Well 16-B	T-189	55	45.4	55	45.4	11	9.1	121
Well 1	T-190	11	9.6	95	83.3	8	7.0	114
Well 10-A	T-191	52	44.4	54	46.2	11	9.4	117
Well 17	T-192	97	42.5	117	51.3	14	6.2	228
Well 3	U-267	18	18.4	7	7.1	73	74.5	98
Well 4	W-267	96	42.3	61	26.9	70	30.8	227

(1) Determined by modified Gutzeit method (spectrophotometric) on digested sample

*% of Total Arsenic

ENCLOSURE NUMBER 4

LEGGETTE, BRASHEARS & GRAHAM
CONSULTING GROUND-WATER GEOLOGISTS

R. M. LEGGETTE
M. L. BRASHEARS
JACK B. GRAHAM
E. T. SIMMONS
S. SIDNEY FOX

551 FIFTH AVENUE
NEW YORK, N.Y. 10017
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CABLE ADDRESS-LEBRAGRA

WATER SUPPLY
DEWATERING
RECHARGING
INVESTIGATIONS
REPORTS

June 18, 1968

Mr. T. Iezzi, Sanitary Engineer
Rohm & Haas Company
Box 219
Bristol, Pennsylvania 19007

Dear Mr. Iezzi:

The following is a general description of the geologic setting of the Tulpehocken Creek watershed in Lebanon and Berks Counties, Pennsylvania, and comments relative to a ground-water divide or hydraulic barrier that we believe is effective in preventing the eastward continuation of ground-water flow in the Lebanon Valley carbonate rocks at Womelsdorf.

The Tulpehocken Creek drainage basin, with an area of a little over 200 square miles, is underlain by shale, carbonate formations composed of limestone and dolomite, and by crystalline rock composed chiefly of granite gneiss. A very minor amount of quartzite occurs adjacent to the crystalline rock. Shales underlie about 55% of the watershed, carbonate rocks about 40% and the crystalline rocks and quartzite about 5%.

The shale, which underlies the northern portions of the watershed, is generally medium gray to dark gray but weathers to a light brownish gray color. Most of the rock is quite fine-grained but there are minor zones or thin lenses of clayey sandstone, pure quartzose sandstone, and platy clayey limestone.

The shale weathers relatively rapidly. The combination of large area of outcrop and tendency to erode results in the largest contribution of suspended solids and bed load to the creek, as compared to other areas of the watershed.

Topographically, the Martinsburg shale forms a region dominated by low, rounded hills and rather ill-defined ridges that run parallel to the strike. The subdued ridges reflect sandstone-dominated areas.

Lithologically, the shale is made up of sandy shale and micaceous fine-grained sandstone. It contains layers that are siliceous, sericitic or carbonaceous. In counties to the east, the formation contains some slate beds but slate was not observed in the Tulpehocken watershed.

June 18, 1968

Mr. I. Iezzi:

The carbonate rocks of the Tulpehocken watershed generally underlie the southern portion of the drainage system. These rocks consist of alternating beds of limestone and dolomite. The beds are aligned in a general east-west direction and are highly folded and faulted.

Typically, the limestone valley is low with slightly rolling topography. The course of Tulpehocken Creek lies in the limestone valley from its headwaters to Womelsdorf where it turns north and flows over the Martinsburg shale formation until it is within a few miles of its mouth. Near its mouth, the creek reenters the limestone terrane.

In an area south of Womelsdorf, about midway between the headwaters and the mouth of the creek, the limestone zone has been deeply buried by an intrusive mass of crystalline rock that has been faulted and thrust over the carbonate rocks. This mass of highly resistant rock forms South Mountain. The bulge of crystalline rocks extends northward into and over the limestone belt at Womelsdorf and Robesonia in such a way that the limestone nearly disappears, being reduced in width to a mile or so.

The carbonate rocks occupy a lowland because they are subject to solution by surface and ground water. In some areas of outcrop of these rocks, there is no obvious surface drainage, indicating that precipitation finds its way to subsurface channels and moves out of such areas as ground-water flow. The contribution of suspended solids and bed load to the creek is minimal in those portions of the watershed underlain by the carbonate rocks.

The flow of Tulpehocken Creek in its upper reaches is somewhat anomalous in that a large limestone quarry discharges an average of about 5,000 gallons per minute into the creek near its origin west of Myerstown. A quantity of finely-divided limestone is contributed to the creek at this point. Other quarrying activity has taken place or is now occurring at several locations farther downstream. The quarries contain limestone of high purity but some clayey and micaceous material is discharged from these operations.

It should be noted that areas underlain by carbonate rocks develop deep soil profiles in many places. These soils consist of the residual products of the weathered rocks. They are clayey, often siliceous, and may have a considerable content of other insoluble residues. However, these soils are not subject to appreciable erosion because of the relatively flat topography and extensive subsurface drainage.

June 18, 1968

Mr. T. Iezzi:

As noted previously, Tulpehocken Creek flows eastward along the axis of the limestone valley to Womelsdorf and then turns northward to a course over an area of Martinsburg shale. This realignment has resulted from the topographic barrier between Womelsdorf and Robesonia formed by the north flank of South Mountain. A remnant of the limestone belt remains in the locality but it is quite narrow. The effect of the resistant crystalline rocks that have partially buried the carbonate has been to shunt the stream farther north.

Our principal interest, of course, is to determine whether the large-scale subsurface flow that characterizes the limestone valley west of this constriction can continue eastward within the limestones and dolomites, or whether essentially all of the subsurface flow finds its path blockaded and is forced out to feed Tulpehocken Creek. Detailed surface flow data and groundwater profiles in the locality are not available, but considerable indirect evidence indicates the existence of a ground-water barrier at this place. We have pointed out previously that the southern boundaries of the watershed are underlain by rocks that would prevent ground-water escape to the south.

There is a low but distinct topographic divide in the limestone belt about half-way between Womelsdorf and Robesonia. No stream crosses this divide nor is there any evidence of underground solution such as sinkholes or solution pits. It appears that the crystalline rocks deepen sharply to the south to depths well beyond the range of typical ground-water circulation for the region. Although the crystalline mass of South Mountain overlies sedimentary formations, including carbonate rocks, the depth may be up to 2,500 feet. Characteristically, solution channels in Lebanon Valley are localized in the upper 300 feet.

In summary, the presently available information concerning groundwater conditions in the Womelsdorf area indicates that ground water moving eastward in the limestones and dolomites of Lebanon Valley encounters an hydraulic divide that essentially conforms to the surface drainage divide between Womelsdorf and Robesonia. If this view is correct, contaminated ground water in the belt of carbonate rocks will not continue to flow eastward past Womelsdorf but will escape by feeding Tulpehocken Creek and continue north and eastward as streamflow over the relatively impermeable shale area.

It is to be noted that stream samples of Tulpehocken Creek do not indicate a pronounced buildup of arsenic below Womelsdorf, but at the same time, we do not have indications that the carbonate aquifers carry a high concentration of arsenic just we

June 18, 1968

Mr. T. Iezzi:

Womelsdorf. The relationship in this respect is inconclusive. Based largely on indirect evidence, it is our conclusion that there is essentially no continuation of contaminated ground-water flow eastward beyond Womelsdorf. Neither is there any likelihood that such water can escape to the south out of the watershed.

Very truly yours,

LEGGETTE, BRASHEARS & GRAHAM

Jack B. Graham

Jack B. Graham

JBG:mm

ENCLOSURE NUMBER 5

Per 6/24 and 6/25 telephone reports from Mr. Kauffman and Mr. Lash, Whitmoyer Laboratories, a sample of Well No. 3 was adjusted to pH 3 and allowed to stand for three days before analysis to determine the effects of low pH on the various forms of arsenic present in the samples. Data follow:

Well No. 3 (Lab. No. W-267)

	Unadjusted pH 7.0		Adjusted pH3	
	ppm	%	ppm	%
Organic As	18	18.4	23	21.7
Inorganic As				
As +5	7	7.1	31	29.3
As +3	73	74.5	52	49.0
Total Arsenic	98	100.0	106	100.0

Additional work of acidifying other well water samples is being done.

T. Iezzi

AR100160